

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 12-Aug-1999		2. REPORT TYPE Technical		3. DATES COVERED (From - To) 11-06-98 to 17-07-99	
4. TITLE AND SUBTITLE Results of Testing a Large Array				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER N00014-99-1-0158	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Claus, Richard, Holton, Carvel and Kostic, Igor, Virginia Polytechnic Institute and State University				5d. PROJECT NUMBER	
				5e. TASK NUMBER Data item #0027	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Virginia Polytechnic Institute and State University, Blacksburg, VA 24061				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) ONR, 800 North Quincy Street, Arlington, VA 22217-5660				10. SPONSOR/MONITOR'S ACRONYM(S) ONR 311	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12. DISTRIBUTION AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Progress report on the development and demonstration of a two-dimensional optical display array constructed of a flexible polymer substrate material with pizeoelectric devices.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 12	19a. NAME OF RESPONSIBLE PERSON Dr. Kenneth L. Reifsnider
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code) (540) 231-9359

19990903 152

Progress for NAVCIITI Program Deliverable Data ItemNo. 0027

Results of Testing a Large Area Array

**Dr. Richard Claus, Carvel Holton, Igor Kostic
Fiber & Electro-Optics Research Center
Virginia Tech**

August 1999

Summary

This task has recently focused on the development and demonstration of an active two-dimensional optical display array. Our goal is to fabricate a large, flexible multi-pixel array on a thin polymer substrate, and incorporate sensing functionality into the material of the array. In this way, finger or stylus pressure, or light from a laser pointer, may be sensed, to allow users to selectively interact with the display.

During the reporting period, we have made progress in the development of the optical display elements on flexible polymer substrate materials, and in the demonstration of piezoelectric devices on similar substrates.

1.0 Executive Summary

Accomplishments during the reporting period include the following items.

- Designed, fabricated and demonstrated a multi-pixel optoelectronic light emitting array on a very thin polyester substrate material.
- Fabricated chemical precursors, formed thin films from these precursors using ESA processing, performed initial characterization of d_{33} of piezoelectric thin films and displacement behavior of electrostrictive thin films.
- Discussed results with cognizant technical personnel in the Chemistry and Optical Sciences Divisions at the Naval Research Laboratory.

2.0 Program Task Technical Goal Review

The overall objective of this task is to develop the basic science capability to form multifunctional electronic, optoelectronic and mechanically active materials and devices by ESA processes, and to apply that technology to related applications involving the integration of similar functionalities and structural substrates. We have chosen interactive light emitting diode (LED) display and detector arrays as initial demonstrators, because they will prove the integrated concepts of mechanical and optical detection and electronic functionality.

So we may achieve this goal, our work is focused in the following areas.

- 1) Development of basic chemical processes for the manufacturing of noble metal and metal oxide nanoclusters, conducting and other polymers, cage structured and other molecules required by desired optoelectronic and mechanically active functionalities,
- 2) Development of the ESA dip-and-wash manufacturing process for fabrication of these thin films and devices directly on structural composites or other flexible substrates, and
- 3) Fabrication, and characterization of the performance, of an optoelectronic display array, with integrated optical detection and mechanical detection, and consideration of how similar mechanical, optical and electronic functionality may be extended to Navy display requirements.

Additional prototyping of related device and material products and analysis of basic nanocluster functionalities are important but less critical program task goals.

3.0 Project Task Review

The technical tasks that we have set to lead us rapidly to device development and potential use in the fleet are summarized as follows.

Task 1 - Consider the requirements of an integrated optoelectronic display or detector array with mechanical and optical detection. This analysis is being used to set material and device specifications and performance goals for the program task.

Task 2 - Extend, optimize and upscale precursor synthesis process. The availability and functionality of these precursors is required to design and ESA-synthesize thin-films with desired properties and functional opto-electronic and piezoelectric and optical detection behaviors.

Task 3 - Analyze ESA synthesis process for multifunctional, multilayered material and device manufacturing. The ESA process consists of alternately dipping a charged substrate into polyionic precursor solutions, and washing the coated substrate between subsequent dipping steps. Through prior research, FEORC has investigated dip and wash process variations and solution chemistries to yield uniform multi-layer thick-films.

Task 4 - Synthesize and evaluate an optoelectronic test article on a flexible substrate. Both LED arrays and photodiode detector arrays will be fabricated on mechanically-active flexible substrates using the design procedure, chemical precursors and process sequence developed above. The ability of the device to emit or detect light will be demonstrated.

Task 5 - Establish application plan with Navy colleagues.

The remainder of this report reviews the ESA process and briefly describes the progress made during the reporting period.

4.0 Review of Accomplishments During Reporting Period

Primary effort during the reporting period has resulted in the following accomplishments.

- 1) Studied methods for the fabrication of passive matrix optoelectronic x-y displays consisting of tens of light emitting elements on a flexible substrate material.
- 2) Demonstrated d_{33} and displacement responses for a range of thin films formed by ESA processing.

This section briefly reviews these accomplishments.

5.0 ESA Optoelectronic Device Improvement

In previous experiments we have fabricated PPV/PMA thin film-based LEDs on ITO-layer-patterned flexible and rigid substrates. We have also have tested the performance of encapsulated ESA-formed LEDs, where the encapsulation provides protection of the polymer films from photo-oxidation and the metallic contacts from oxidation. The results obtained and discussed in prior publications by FEORC researchers indicate that such environmental sealing can effectively prolong device operation. In addition, we have used calcium, which has a relatively low work function, to replace aluminum, as the cathode contact material on initial LED prototype devices. The result of this material replacement has been that, as anticipated, the operational bias voltage required for the operation of the device is dramatically decreased. Such a voltage decrease is desired for commercial LED and other devices.

A key advantage of organic light emitting diodes (OLEDs) is the potential for fabricating large-scale two-dimensional displays and detection arrays at low cost for commercial applications. Our prior work has demonstrated the ability to form reasonably large-scale (10 cm x 15 cm) single element displays using ESA formed thin films. In practice, it is also very important to develop multi-element OLED matrices, in which each OLED element in the two-dimensional array has video-rate switching speed. In such devices, the individual OLED elements may be positioned at the geometric intersections of the addressed pairs of anodes and cathodes.

During this reporting period, we have thus developed and demonstrated this additional geometry of display, specifically an OLED element matrix on a mechanically flexible polyester thin film substrate. The choice of this type of substrate was determined by the requirement of combining optoelectronic functionality and mechanical motion in a single device. The thin flexible substrates used here as the base materials for light emitting devices are identical to some of the substrates, described below, that have been used to form flexible actuated demonstration test articles.

Flexible polyester substrates, (35 mm)² in area and coated with electrically conducting and optically transmissive electrodes, were used to fabricate the OLED matrix pixel arrays.

On the surface of the substrate, eight ITO thin films strips, each 3-mm wide, were fabricated with a pitch of 4 mm, as shown in the diagram in Figure 5-1. After the substrate with the patterned ITO conducting electrode layer was formed, and the substrate was chemically cleaned, and 25 bilayers of PPV precursor/PMA were synthesized by the ESA process.

The resulting multilayer thin film was then heated under vacuum, by the sublimation process reviewed in prior task program reports, to convert the PPV precursor into active conjugated PPV. Additionally, a layer of Alq3 was then formed on the top

surface of the multilayer film to provide balanced carrier injection into the active region of the LED.

Finally, the vacuum deposition of thin film aluminum column cathodes, oriented perpendicular to the ITO strips was performed under a pressure of 10^{-6} torr, through a comb-shaped shadow mask. The resulting 7 element x 8 element LED matrix display is shown in three sections of Figure 5-2. Here we specifically show the flexible multielement array (Figure 5-2a), and two adjacent rows of elements in the array in the "on" state (Figure 5-2b).

The bias voltage applied to each of the pixels in the "on" state was 10 V. Light emission from the pixels was clearly visible under normal room lighting conditions. However, due to the relatively high work function of the aluminum metal electrodes that were employed during these tests to simplify array fabrication, pixel efficiency was not as high as that observed with individual Ca cathodes, as anticipated. Even without any electromagnetic interference (EMI) insulating thin film buffer layers between the adjacent ITO strips and the Al cathodes, no cross talk between adjacent OLED pixels

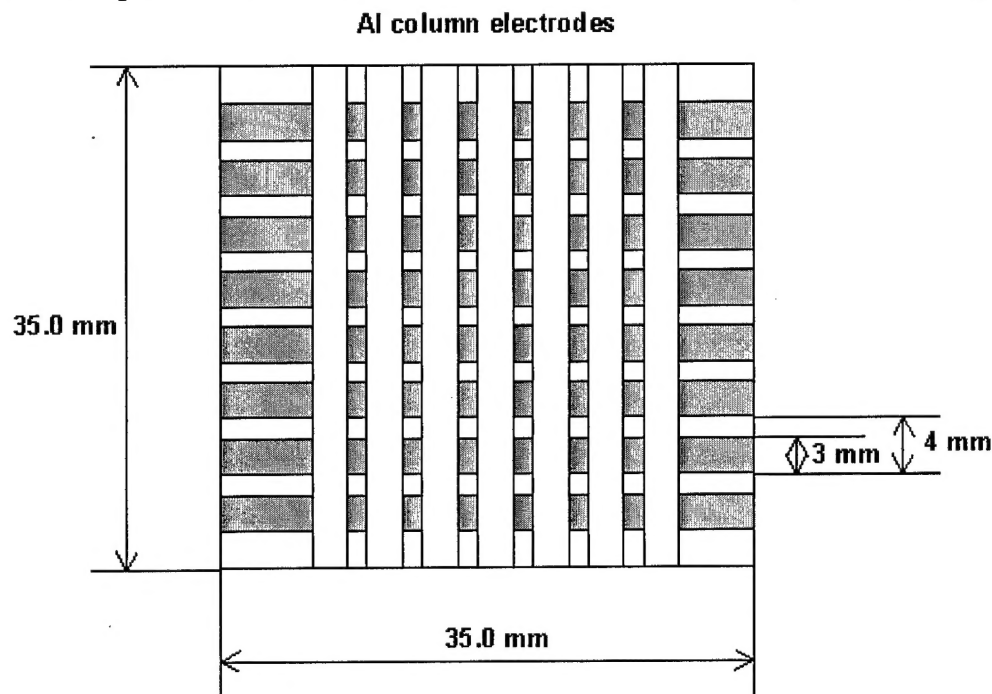


Figure 5-1. Schematic Structure of the Passive OLED's on a Flexible Substrate.

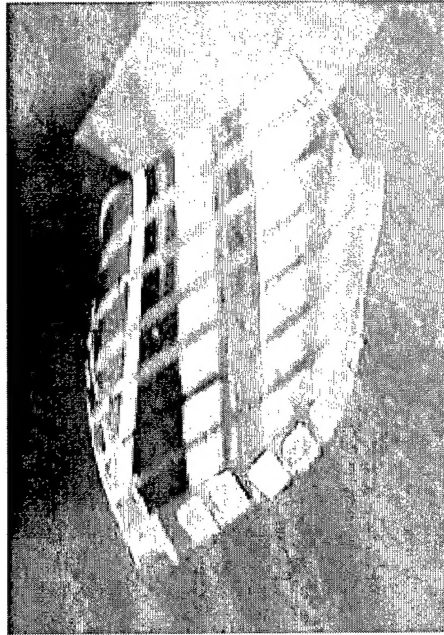


Figure 5-2a. Fabricated OLED Matrix Array on Flexible Substrate.

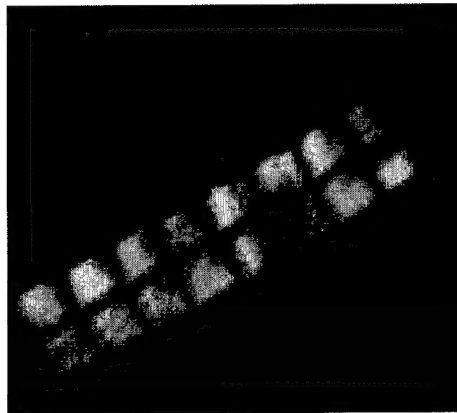


Figure 5-2b. Two Adjacent Rows of LED Elements in "On" State.

was observed. In principle, such a matrix of independently switched optical elements is able to display dynamic patterns such as rapidly changing alphanumeric symbols, by changing the currents applied to each column electrode. These signals may be modulated synchronously using conventional row-electrode scanning, in accordance with the required luminance data for each pixel within the array. These results also suggest the avoidance of crosstalk in multielement detector arrays that are currently under consideration.

The current/voltage characteristic and output luminance versus applied DC voltage were measured for representative individual pixels in the two-dimensional matrix

array. Nominal results of these measurements are shown in Figures 5-3.

I-V curves have been measured for several pixels in the matrix. All of them are essentially identical, which suggests that uniformity of pixel response over the matrix has been achieved and that each pixel can be accessed individually to form a larger two-dimensional display. The brightness of each pixel is comparable to that of those of the individual LEDs with similar structures fabricated previously. This also suggests that identical element to element response should be anticipated for ESA-formed multielement detector arrays.

In summary for this program task, during the reporting period, we have demonstrated the formation of passive matrix OLED arrays on flexible substrates. Of particular importance, excellent uniformity has been achieved over the pixel array, which suggests that each pixel may be accessed individually. Although only a limited number of pixels are shown in the test articles illustrated above, this work has demonstrated the possibility of fabricating passive matrices with larger numbers of pixels and thus higher spatial resolution, based on the luminescent polymer multilayer films prepared by ESA technique. This similarity proves the feasibility of fabricating and interconnecting arrays of other optoelectronic and supporting electronic functionalities into more complex optoelectronic circuits and systems.

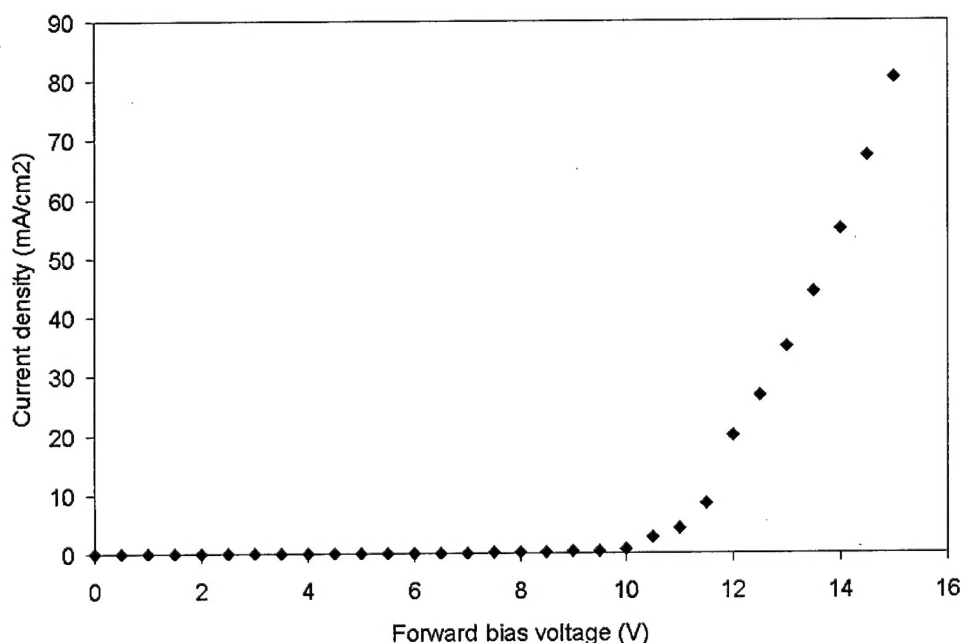


Figure 5-3. Current-Voltage Curve for One Pixel in the OLED Matrix.

6.0 Results with Synthesis of Mechanically Active Thin Films by ESA Processing

During the reporting period, we have also successfully fabricated mechanically active ultrathin composite films through a modified form of the basic ESA process. Polymers

with noncentrosymmetric structures and large molecular dipole moments were selected as initial candidates for synthesis. Inorganic nanoclusters were also utilized in combination with the polymers to form composite films. Table 6-1 lists the materials and substrates used for the self-assembly process in our experiments.

Table 6-1. Materials for fabricating piezoelectric thin films by ESA process.

<u>Materials</u>	<u>Charge property</u>	<u>Solvent</u>
Polymer 1	Negative	water
Polymer 2	Negative	water
Polymer 3	Negative	water
Polymer 4	Negative	methanol: water
PDDA	Positive	water
nanocluster 1	Positive	water
nanocluster 2	Positive	water
Silicon p-111 substrate	Negative	---
ITO-coated glass substrate	Negative	---
Al-coated flexible polymer substrate	Negative	---

Characterization of the piezoelectric ultrathin films were carried out by UV-visible spectroscopy and thickness measurements, film quality was observed by AFM, and the investigation of the electrostrictive and piezoelectric responses was performed by bending deformation experiments and the measurement of piezoelectric coefficients.

We are currently evaluating piezoelectric coefficients of different materials and will report results in the next report.

7.0 Bibliography of Recent Related FEORC Technical Publications and Presentations

The following are recent or current publications or presentations by the research team concerning the ESA processing of multifunctional thin-films and devices.

- [1] Y. Liu, Y-X. Wang and R. Claus, "Layer-by-layer ionic self-assembly of Au colloids into multilayer thin films with bulk metal conductivity," *Chemical Physics Letters*, 298 (1998), p. 315-319, 18 December 1998.
- [2] Y. Liu and R. Claus, "Strong enhancement of optical absorbance from ionic self-assembled multilayer thin films of nanocluster Pt and polymer dye," *Journal of Applied Physics*, Vol. 85, No. 1, 1 January 1999, p. 419-424.
- [3] J. Heflin, C. Figura, D. Marciu, Y. Liu and R. Claus, "Thickness dependence of second-harmonic generation in thin films fabricated from ionically self-assembled monolayers," *Applied Physics Letters*, Vol. 74, No. 4, 25 January 1999, p. 495-497.

- [4] Aprillya Rosidian, Y. Liu and R. Claus, "Ionic self-assembly of ultrahard ZrO₂/polymer nanocomposite thin films," *Advanced Materials* 1998, 10, No. 14, p. 1087-1091.
- [5] K. Lenahan, Y-X. Wang, Y. Liu, R. Claus, J. Heflin, D. Marciu and C. Figura, "Novel polymer dyes for NLO applications using ISAM technology," *Advanced Materials* 1998, 10, No. 11, p. 853-855.
- [6] Y. Liu, A. Rosidian, K. Lenahan, Y-X. Wang, T. Zeng and R. Claus, "Characterization of electrostatically self-assembled nanocomposite thin films," *Smart Materials and Structures* 8 (1999), p. 100-105.
- [7] Y. Liu, W. Zhao, F. Zhang and R. Claus, "ESA of Pt Nanoclusters into 3-D Highly-Conductive Multilayer Arrays," submitted to *Advanced Materials*, April 1998.
- [8] Y. Liu and R. Claus, "Conductivity Effects in Self-Assembled Magnetic Thin-Films," Invited Paper, *Proc. MRS*, Fall Meeting (Boston), December 1997.
- [9] Y. Liu and R. Claus, "GMR of Electrostatically Self-Assembled Fe₃O₄ Nanocluster and Polymer Thin Films," submitted to *IEEE Trans. on Magnetism*.
- [10] J. R. Heflin, Y. Liu and R. Claus, "Noncentrosymmetric Ionically Self-Assembled Thin Films for Second Order Nonlinear Optics," *Proc. QELS Conf.*, Baltimore, June 1997.
- [11] W. Zhao, Y. Liu, Y.-X. Wang and R. Claus, "Strong Enhancement of ESA LED Emission," submitted to *J. Appl. Phys.*
- [12] R. Claus and Y. Liu, "Multilayer Films Based on Ionic Self-Assembly," DARPA/DSRC Workshop on Multilayer Structures, La Jolla, CA, July 1998.
- [13] Y. Liu, A. Wang and R. Claus, "Molecular Self-Assembly of TiO₂-Polymer Nanocomposite Films," *J. Physical Chemistry B* 1997, **101**, 1385-1388.
- [14] Y. Liu and R. Claus, "Blue Light Emitting Nanosized TiO₂ Colloids," *J. Am Chem. Soc.*, **30**, no. 22, May 1997.
- [15] R. Claus and Y. Liu, "Self-Assembled Nanoparticle-Based Thin-Film Materials and Devices," Invited Seminar, Institute for Defense Analyses (Alexandria, VA), Nov. 1997.
- [16] R. Claus and Y. Liu, "ESA Processes for Thin Film Materials Fabrication," WPAFB Polymer Seminar, May 1998, invited.

- [17] Y. Liu, "Characterization and Patterned Ionic Polymer Films from a Novel Self-Assembly Process," Ph.D. dissertation, Virginia Tech, 1996.
- [18] Y. Liu, A. Wang and R. Claus, "Layer-by-Layer Electrostatic Assembly of Nanoscale Fe_3O_4 Particles and Polyimide on Silicon and Silica Surfaces," *Appl. Phys. Lett.* **71** (16), 20 October 1997, 2265-2269.
- [19] Y. Liu and R. Claus, "Optical, Electronic, Magnetic and Mechanical Thin Films and Devices Based on Ionic Self Assembly," Innovations in Materials Conference, Washington, DC, July 1998.
- [20] Y. Liu and R. Claus, "Enhanced Conductivity in ESA-Formed Ultrathin Films," ICAST Conference, Cambridge, MA, October 1998.
- [21] Y. Liu, R. Claus, K. Lenahan and Y-X. Wang, "Electrostatically Self-Assembled Electronic and Photonic Devices on Polymer Substrates," MRS Fall Meeting, Boston, December 1998.
- [22] K. Lenahan, "Nonlinear Optical Materials and Devices Synthesized by ESA," Ph.D. dissertation, Virginia Tech, May 1999.
- [23] Y. Liu, R. Claus, K. Lenahan and Y-X. Wang, "Electrostatic Self-Assembly of C_{60} Thin Films," MRS Fall Meeting, Boston, December 1998.
- [24] Y. Liu, A. Rosidian and R. Claus, "Mechanical Properties of Electrostatically Self-Assembled $\text{Al}_2\text{O}_3\text{-ZrO}_2$ Nanocomposites Prepared at Room Temperature," submitted to *Appl. Phys. Lett.*, August 1998.
- [25] Y. Liu, R. Claus, Y-X. Wang, W. Zhao and K. Lenahan, "Electrostatic Self-Assembly of Electronic and Photonic Devices on Polymer Substrates," Proc. MRS Conference Boston, December 1998.
- [26] Y. Liu, Y.-X. Wang, H. Lu and R. Claus, "Formation of Multilayer Fullerene Films by Electrostatic Self-Assembly" submitted to MRS Spring Meeting, San Francisco, April 1999.
- [27] F. Zhang, Y. Liu and R. Claus, "Fabrication and Structure of Electrostatically Self-Assembled Soft Magnetic Thin Films," submitted to MRS Spring Meeting, San Francisco, April 1999.
- [28] A. Rosidian, Z. Luo, Y.-X. Wang, W. Zhao, Y. Liu and R. Claus, "Dielectric Properties of Nanocluster/Polymer Thin Films Formed by Electrostatic Self-Assembly," submitted to MRS Spring Meeting, San Francisco, April 1999.

- [29] "Ultrahard ZrO₂/Polymer Thin Films Based on Ionically Self-Assembled Monolayer Processes," A. Rosidian, R. Claus, Y. Liu, ASM Materials Solutions Conference, Rosemont, IL, 12-15 October 1998.
- [30] "Room Temperature Fabrication of Transparent ZrO₂/Polymer Nanocomposite Thin-Films with Controlled Thickness by the Ionic Self-Assembled Monolayer Method," A. Rosidian, Y. Liu and R. Claus, American Vacuum Society (AVS) Meeting, Baltimore, November 2-6, 1998.
- [31] "Synthesis of Piezoelectric Thin Film Materials by ESA," Y. Liu, W. Zhao, Y.-X. Wang and R. Claus, American Society for Nondestructive Testing Conference, Nashville, 19-23 October 1998
- [32] "Ultrahigh Conductivity Nanocluster-Based Thin Film Electrode Interconnects for Sensors and Actuators," Y. Liu, W. Zhao, Y. Wang and R. Claus, American Society for Nondestructive Testing Conference, Nashville, 19-23 October 1998.
- [33] "Advanced Sensors and Thin Film Materials for System Identification and Health Monitoring," R. Claus and K. Lenahan; invited, and sponsored in part by the National Science Foundation, Workshop on Nonlinear Identification and Health Monitoring, Honolulu, 30-31 October 1998.
- [34] R. Claus and W. B. Spillman, "Sensory Phenomena," SPIE Smart Materials and Structures Conference, Newport Beach, CA, 1-4 March 1999.
- [35] F. Arrugi, R. Claus, Y. Liu, I. Matias and K. Lenahan, "Self-assembled optical fiber sensors," SPIE Smart Materials and Structures Conference, Newport Beach, CA, 1-4 March 1999.
- [36] Y.-X. Wang, A. Rosidian, Y. Liu and R. Claus, "Self-assembled flexible electrodes on electroactive polymer actuators," SPIE Smart Materials and Structures Conference, Newport Beach, CA, 1-4 March 1999.
- [36] K. Lenahan, R. Claus and Y. Liu, "ESA processes for linear and nonlinear multilayer filters," SPIE Smart Materials and Structures Conference, Newport Beach, CA, 1-4 March 1999.
- [37] K. Lenahan, Y. Liu, Y.-X. Wang, R. Claus, "ESA processes for noncentrosymmetric thin films and devices," SPIE Smart Materials and Structures Conference, Newport Beach, CA, 1-4 March 1999.
- [38] Y. Liu, A. Rosidian, R. Claus, "Formation of ultrahard metal oxide cluster coatings by ESA," SPIE Smart Materials and Structures Conference, Newport Beach, CA, 1-4 March 1999.

- [39] Y. Liu and R. Claus, "Electrostatic self-assembled metal nanocluster thin films with bulk material conductivity," SPIE Smart Materials and Structures Conference, Newport Beach, CA, 1-4 March 1999.
- [40] A. Rosidian, Y. Liu, W. Zhao and R. Claus, "Ultracapacitors formed by molecular self-assembly," SPIE Smart Materials and Structures Conference, Newport Beach, CA, 1-4 March 1999.
- [41] Y. Liu, R. Claus, K. Lenahan, W. Zhao and T. Zeng, "Electrostatically self assembled thin film materials and polymer actuators," American Society for Nondestructive Evaluation Spring Meeting, Orlando, FL, 22-26 March 1999.
- [42] Y. Liu, R. Claus, A. Rosidian, T. Zeng, "A new route to prepare hard and antiscratch coatings at room temperature," Materials Research Society Spring Meeting, San Francisco, CA, 4-9 April 1999.
- [43] F. Zhang, Y. Liu and R. Claus, "Layer-by-layer self-assembled soft magnetic thin films with controlled magnetic properties," Materials Research Society Spring Meeting, San Francisco, CA, 4-9 April 1999.
- [44] Y. Liu, Y-X. Wang, X. Lu and R. Claus, "Multifunctional fullerene films for photonics," Materials Research Society Spring Meeting, San Francisco, CA, 4-9 April 1999.
- [45] Y. Liu, R. Claus, J. Heflin, D. Marciu, C. Figura, "High speed layer-by-layer self-assembly of polarized chromophoric superlattices," Materials Research Society Spring Meeting, San Francisco, CA, 4-9 April 1999.
- [46] K. Lenahan, Y. Liu, Y-X. Wang, R. Claus, "ESA of multilayer noncentrosymmetric thin films and devices," Materials Research Society Spring Meeting, San Francisco, CA, 4-9 April 1999.